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Rational Design and Synthesis of Multifunctional Nanostructures for Biological and Medicinal Applications

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~~*Rational Design and Synthesis of Multifunctional Nanostructures for Biological and Medicinal Applications*~~

~~Mesoporous nanomaterials (silica) can be rationally designed for various applications. More specifically they can be used in catalysis, biosensing, and bioseparation applications and site specific drug delivery. In this experiment Mobile Crystalline Material, MCM-41, was used to for the adsorption and release of rhodamine 6G and ibuprofen. Successful modification of MCM-41 proved that the properties of the functional groups affect the adsorption of compounds into the pores of this material. In separate studies silica core-shell nanostructures were explored. Layers of gold nanoparticles successfully adhered to the shells which were then encased in silica shells. When further developed modified silica spheres can potentially be used in bioimaging applications.~~

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The Design and Synthesis of Functionalized Nanoporous Materials for Adsorption and Controlled Release of Drugs

Amy N. Otuonye**, Gang Wang, Elizabeth A. Blair, Kelly Denton, Nicauris Batista and Tewodros Asefa*

CHAPTER 1

Studies of adsorption and release of rhodamine 6G and ibuprofen

Abstract

Mobile Composite Material's (MCM-41) was modified by the addition of various functional groups, which increase the materials efficiency for an assortment of applications. Mesoporous materials have demonstrated to be capable of adsorbing and releasing of model drug molecules, rhodamine 6G and ibuprofen. Mesoporous silica

materials functionalized with mercaptopropyltrimethoxysilane (MPTS), vinyltrimethoxysilane (VTS), aminopropyltrimethoxysilane (APTS), and N-(2-animoethyl)-3-aminopropyltriethoxysilane (AAPTS) were used to test the adsorption and release of rhodamine 6G (R6G) and ibuprofen. The vinyl and mercaptopropyl groups adsorbed and released more rhodamine 6G than the primary and secondary amine groups. The adsorption and release of ibuprofen was the opposite of the R6G experiment with the primary and secondary amine groups, which were found to be the only samples to adsorb and therefore release ibuprofen.

Introduction

Methods of delivering drugs into the body are not completely efficient. There are many problems with harmful side effects such as organ damage, rashes and other skin irritations. Due to this problem there have been various studies to improve the transport of drugs. One involves a

method for manufacturing drug delivery materials that hold the therapeutic agent in a shell, combining the first composition method with a sol and then converting the mixture into a solid or semi-solid drug delivery material.[1] Another engages self-assembled polymeric micelles whose unique core shell structure, small size and adjustable surface make it a potential drug delivery agent. It may also be used in applications with tumor targeting and gene therapy.[2] Mesoporous nanomaterials such as MCM-41 have been considered as candidate materials for adsorption and release of drug molecules. MCM-41 is a nonporous material with hexagonally ordered tube-like porous structures that has high surface area, and has large storage capacity mesoporous silicate, which makes a good candidate for drug delivery. The advantages of this material are that it has large surface area and ordered nanometer pore structure, that can be modified with various functional groups. Furthermore, it can be synthesized with less costly synthetic procedures. MCM-41 has the potential to lengthen the circulation time of the drug in the body and can also

act as a shell to shield the drug from physiological milieu. This material can be useful in cancer therapy because even though they are “nano” they are still larger than the size of the pores in the walls of the vascular endothelium. The particles can then selectively accumulate in the site of the tumor where the vasculature is leaky.

Mesoporous materials also have great potential in of ion exchange, catalysis and sensing applications. Many efforts have been made to tailor the pore size, structure and surface of these materials for those applications purposes. Pore size depends on the type of surfactant that was used during synthesis. Therefore as the chain length of the surfactant increases so does the pore size. Although pore size does have an effect on drug delivery, many methods have focused on the modification of the structure of the mesoporous materials by introducing various functional groups to the surfaces of the pores with various routes.[3,4]

Optimization of drug efficacy and reduction of unfavorable effects is the aim of controlled drug release. A few studies have shown that proper timing of the administration of drugs and controlled drug release can lead to the reduction of undesired effects and pharmacokinetics[4] The first chapter discusses the modification of MCM-41 with different organic functional groups for the adsorption of rhodamine 6G and ibuprofen. Varying the chemical group attached to the surface varied the compounds that were adsorbed which can consequently lead to controlled release of that substance. Functionalization of the inner walls of MCM-41 can indeed affect the strength of interaction between the drug molecules and the materials and consequently, the rate of release of the drug.

Uniform size pores with silanol groups can host a variety of polymers, semiconductor clusters and organic molecules.[5] These silanol groups were obtained after extraction of the surfactant from the inner channels of MCM-41. Further studies were

performed on functionalizing mesoporous nanomaterials. Replacing the silica precursor (tetraethylorthosilicate TEOS) with organosilanes can increase the non-covalent interactions between the drug and the material. Hydrophobic and hydrophilic properties of the functionalized groups help determine pore selectivity[6]. Thus far MCM-41 has shown promising results in adsorption and release studies. It has demonstrated the adsorption and release of a model drugs, rhodamine 6G and ibuprofen.

EXPERIMENTAL METHODS

Materials

Ammonium hydroxide, hydrochloric Acid (HCl) and the Whatman-1 filter paper were both obtained from Fisher Scientific. Hexadecyltrimethyl ammonium bromide (CTAB), methanol, tetraethylorthosilicate (TEOS), rhodamine 6G and ibuprofen sodium salt were all obtained from Sigma-Aldrich. The functional

groups mercaptopropyltrimethoxysilane (MPTS), vinyltrimethoxysilane (VTS), aminopropyltrimethoxysilane (APTS), and N-(2-animoethyl)-3-aminopropyltriethoxysilane (AAPTS) were obtained from Gelest and used without further purification.

Characterization tools

The Perkin Elmer Lambda 950 UV-Vis-NIR Spectrophotometer was used to measure the UV-Vis absorbance spectra. It was used to analyze the amount of rhodamine 6G that was in the supernatant liquid. A decrease in absorbance indicated an increase in adsorption of the dye. The less dye in the supernatant liquid the more dye was adsorbed by the functionalized samples. Nitrogen gas adsorption is widely used to analyze mesoporous material. It utilizes a mathematical formula that was developed by three men Brauner, Emmett and Teller (BET). BET gas adsorption was measured using a Micromeritics Tristar-3000 BET instrument. This machine was used to determine the surface

area and pore width of the mesoporous material. Thermogravimetric Analysis (TGA) was performed with a Q-500 Quantachrome Instrument (TA-Instruments). It was used to determine the amount of surfactant was in the sample.

Synthesis of MCM-41- the aging method

A solution of 33.40 mL distilled water and 15.00mL ammonium hydroxide was prepared and 0.84 g CTAB was dissolved in it by stirring. Then, a mixture of 4.00 g TEOS was added. The solution was stirred at room temperature for 2 h and then stored in oven at 80 °C for 2 days (48 h). The sample was cooled down and filtered with Whatman-1 filter paper. The solid was washed thoroughly with large amount of distilled water and dried under ambient condition.

Extraction of MCM-41 and functionalization of MCM-41

2 g of the functionalized mesostructured material was placed in a solution of 50 mL

methanol and 10 mL HCl for 5 h at 50 °C. The solution was filtered with Whatman-1 filter paper and the solid was then washed three times with 20 mL methanol and dried under vacuum for 30 min.

500 mg of extracted mesoporous silica was then mixed with 250 ml of ethanol at 80°C. 2.94 mmol of organosilane including mercaptopropyltrimethoxysilane (MPTS), vinyl trimethoxysilane (VTS), 3-aminopropyltrimethoxysilane (APTS), or N-(2-Aminoethyl)-3-aminopropyltriethoxysilane (AAPTS), was added to the solutions. Four samples of mesoporous materials were produced. Each sample was functionalized with only one organosilane.

Adsorption and Release of Rhodamine 6G

0.35 µM of rhodamine 6G (R6G) was prepared with distilled water. All functionalized samples were placed in R6G solution until they were fully saturated. Simulated Body Fluid (SBF) was prepared as in literature[2]. The pH was adjusted

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by adding HCl. Each of the filtered Rhodamine 6G samples was placed in 100 mL SBF of pH 7.4 and temp 36.5^{o}C. The supernatant for each solution was tested. The wavelength was monitored at ~526 nm. The experiment was completed when there was no change in the absorbance at ~526 nm.

Adsorption and Release of Ibuprofen

Ibuprofen was made from 8.00 g of ibuprofen sodium salt and 800 mL of 1M hydrochloric acid (HCl). The product (ibuprofen) was then purified by recrystallization and washed with acetone to remove any further impurities. After drying, 400 mg of the purified ibuprofen was dissolved in 400 mL ethanol (1 mg/mL ratio). Then 25 mL of the ibuprofen / ethanol solution was placed in 0.1 g of each sample of mesoporous material that was modified with 3-mercaptopropyltrimethoxysilane (MPTS), vinyltrimethoxysilane (VTS), 3-aminopropyl trimethoxysilane (APTS), and N-(2-animoethyl)-3-aminopropyl triethoxysilane (AAPTS). To test the release of ibuprofen, 100 mL of SBF was poured

into the filtered samples of ibuprofen concentrated functionalized samples.

RESULTS and DISCUSSION

Bottom-up approach was used to synthesize this mesoporous material. This synthetic approach involved the self assembly of micelles as a template. Micelles are the aggregation of molecules which typically have hydrophobic tails and hydrophilic heads. This template was later extracted to create channels for further experimentation. The extraction reaction resulted in the creation of silanol groups on the walls of the mesoporous silica which was later be modified through a process known as functionalization.

The synthesis of functionalized MCM-41 using CTAB micellar templates produced nanoporous silica microspheres with hexagonally ordered tube-like porous structures. The template

was extracted using the above stated method. The products were mesopore channels tubes with hydroxyl groups dispersed on the wall.

Synthesis of Mesoporous Silica

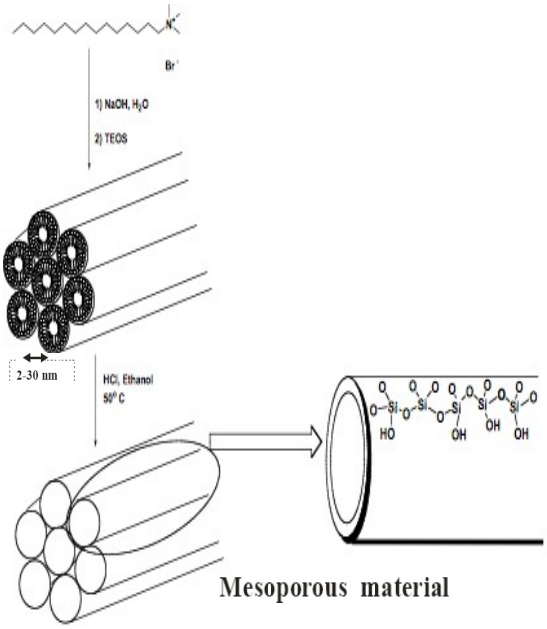

Figure 1. The above displays the synthesis and extraction of MCM-41.

A bottom-up approach was used to synthesize this mesoporous material. This synthetic approach involved the self assembly of micelles as a template. Micelles are the aggregation of molecules which typically have hydrophobic tails and

hydrophilic heads. This template was later extracted to create channels for further experimentation. The extraction reaction resulted in the creation of silanol groups on the walls of the mesoporous silica, which were later be modified through a process known as functionalization. The extracted samples were then analyzed using a BET nitrogen gas adsorption.

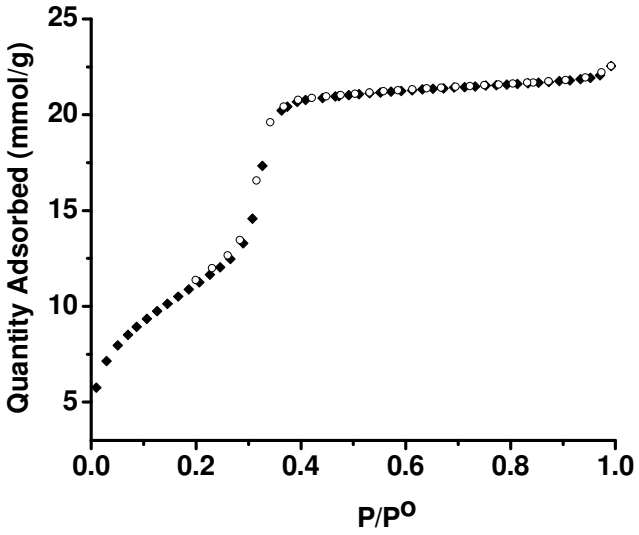

Figure 2. The above is a spectrum obtained from BET analysis.

The spectrum is a nitrogen gas adsorption isotherm (Type IV) obtained for surface area and

pore size distribution analysis of mesoporous material. The BET surface area observed for the mesoporous material was 918 m^2/g. This is a high surface area for such a material. The measured BJH pore width of 2.9 nm was within the range of that of a mesoporous material.

Thermogravimetric Analysis of Mesoporous Material
Shows the loss of surfactants

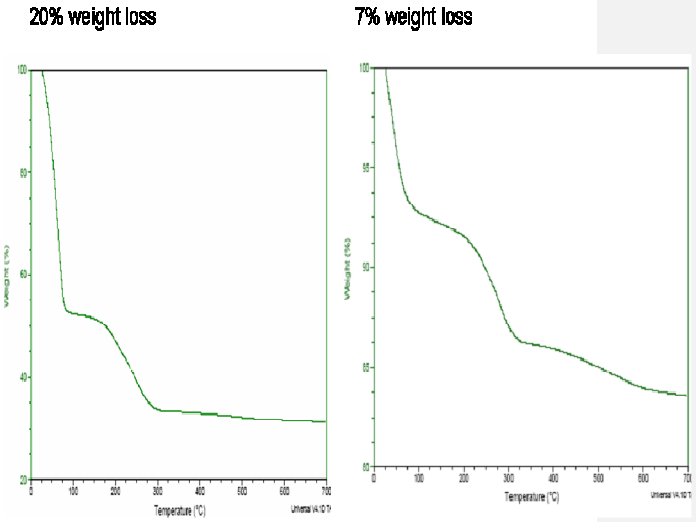

Figure 3. The above displays the results from unextracted and extracted MCM-41.

The TGA experiments showed a weight loss of 20% for unextracted MCM-41 and a 7% weight loss between 100 – 300 °C for the extracted sample. The weight loss below 100°C was due the presence of physisorbed water. Loss of the surfactant was detected between 100°C and 400°C. The higher weight loss was due to the higher concentration of surfactant in the mesoporous material. Comparatively a lower weight loss indicated less surfactant in the mesoporous silica.

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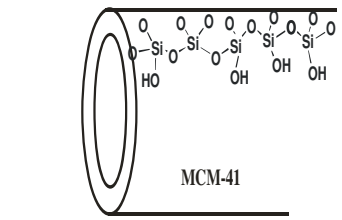
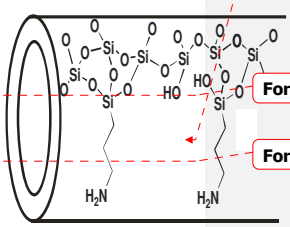
Mesoporous silica was synthesized using the aging method and functionalized with four different functional groups. Functionalization (grafting) is the use of various chemical groups to modify the surface of the mesoporous silica. The groups used were 3-mercaptopropyl trimethoxysilane (MPTS), vinyltrimethoxysilane (VTS), 3-aminoproplyltrimethoxysilane (APTS), N-(2-aminoethyl)-3-aminoproplytriethyoxysilane (AAPTS). An example of the scheme for functionalizing MCM-41 with APTS is displayed in Scheme 1, below.

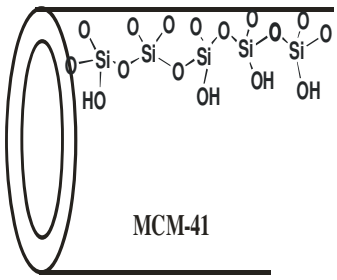
Scheme 1. Scheme of functionalization of APTS with ethanol.



EtOH, APTS

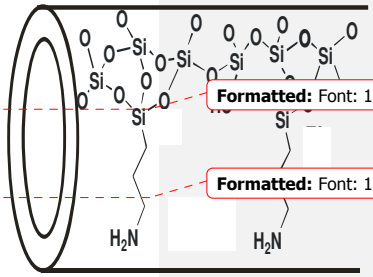
Reflux, 6hr





EtOH, APTS

Reflux, 6hr



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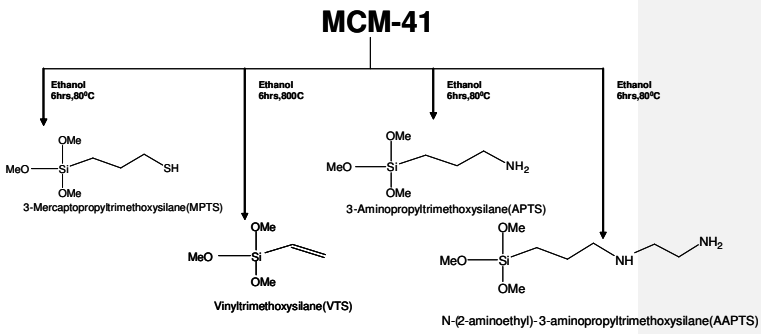
Ethanol was used because it has been previously shown that it produced a spatially

dispersed arrangement of organosilanes (amino groups) unlike solvents like toluene which produces corrugated functional groups in the mesoporous silica. Ethanol was the solvent used to graft the other three functional groups in MCM-41.

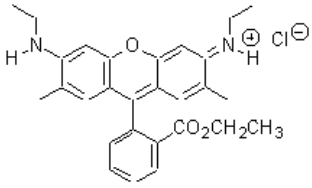
Scheme 2. Scheme for functionalization of MCM-41 and organosilane structures.



The four groups, MPTS, VTS, APTS and AAPTS were chosen to test the effects of hydrophobicity and hydrophilicity of the functionalized mesoporous silica in relation to the adsoption of the R6G and ibuprofen. The addition of VTS incorporated a double bond into the silica. MPTS added a long chain and an –SH group. The

samples produced by these two groups were more hydrophobic than those produced by the amine groups. APTS added a primary amine group and AAPTS, along with a long chain, integrated a secondary amine to the surface of the silica. These groups were more hydrophilic than MPTS and VTS. The grafted samples were then used for the drug adsorption and release studies with rhodamine 6G and ibuprofen.

Rhodamine 6G (R-6G)



MPTS VTS APTS AAPTS

Figure 4. The structure of R-6G and the saturated samples are shown.

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Rhodamine 6G is a fluorescent compound with various chemical properties. It is dark pink in color and contains different functional groups. It has ionic properties because it dissolves in water, but a majority of the structure is hydrophobic, as is seen from its multiple benzene ring structures. This compound was chosen because it can be easily monitored by UV-Vis absorption spectroscopy.

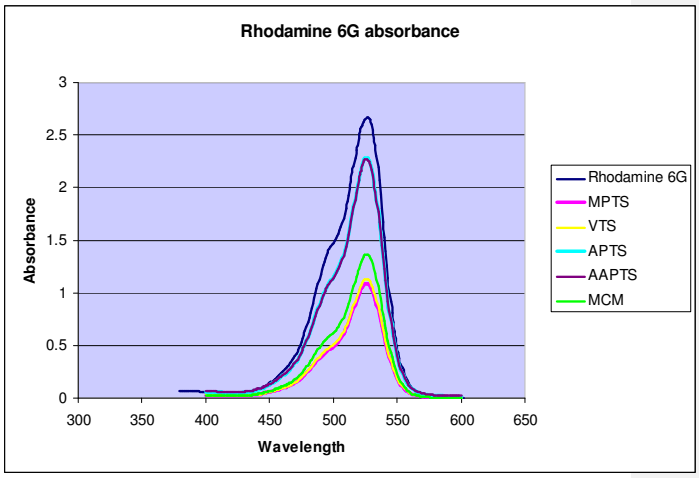

Figure 5. Absorption of rhodamine 6G by MCM-41 compared with the four grafted samples.

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Each grafted mesoporous silica sample was placed in a 0.35 μM solution until they were fully saturated. From Figure 4 it is apparent that some of the saturated samples are lighter solutions are lighter than others. The MPTS and VTS samples appeared deep pink while those from the amine samples appeared light pink. The lighter the supernatant the greater the concentration of the solute was in the functionalized samples. The same properties were observed. The samples that absorbed more R6G released more of the substance.

The supernatant of each sample was tested and compared to the absorbance of R6G. AAPTS and APTS had the closest absorbance to the absorbance of R6G. The VTS and MPTS functionalized samples had the lowest absorbance. This shows that as the samples adsorbed more R6G and the supernatant contained less R6G which produced a lower absorbance.

While all the samples adsorbed R6G, VTS and MPTS adsorbed more of the substance than APTS and AAPTS. There could have been less of an interaction between the amine groups, in the mesoporous surface, and R6G. This then means that there was a stronger interaction between the samples grafted with VTS and MPTS and R6G, which may have been caused by the hydrophobic interaction between the functional groups and hydrophobic parts of R6G. These results show that functional groups greatly influence the adsorption of R6G into mesoporous materials.

The release of rhodamine 6G was performed in Simulated Body Fluid (SBF). All samples

released R6G into SBF but the samples that adsorbed more released more R6G (MPTS and VTS). Adsorption and release experiments were then tested with ibuprofen, an anti-inflammatory drug. Although it is not easily soluble in water it is a commonly used drug that was used to test the properties of the functionalized materials.

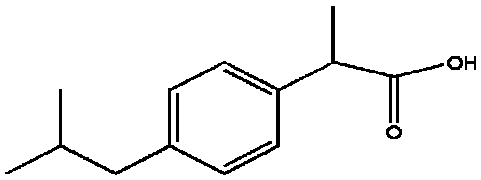

Figure 6. *Structure of ibuprofen*[3]

Ibuprofen, on the other hand, is an anti-inflammatory drug. Other members of this class include aspirin, naproxen (Aleve), nabumetone (Relafen), indomethacin (Indocin), and several others. This drug was chosen because it is easy to probe and has previously been used adsorption and release studies. The mesoporous silica samples functionalized with APTS, and AAPTS, were shown to be useful as potential ibuprofen carriers

although these samples were not as effective in adsorbing rhodamine 6G.

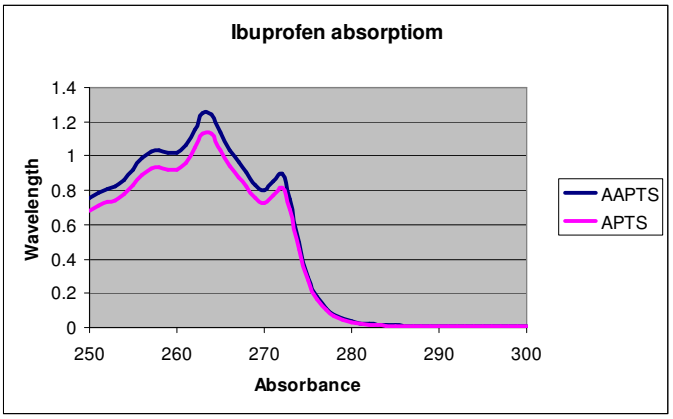

Figure 7. The graph displays the adsorption of ibuprofen by each grafted sample with respect to time.

The results from the ibuprofen experiment varied from those of R6G because the structure of both compounds and interaction with functional groups were very different. The result was ibuprofen was adsorbed in the samples that were grafted with APTS and AAPTS and not in the samples grafted with MPTS and VTS. AAPTS had the higher absorbance value. Since the supernatant

of each solution was tested, AAPTS samples then adsorbed less ibuprofen that the APTS samples. This favorable adsorption of ibuprofen may be due to interaction of the amine groups and the acidic groups of ibuprofen (~~f~~Figure 6). The release of ibuprofen was performed on APTS and AAPTS (the only two samples to absorb ibuprofen). Simulated body fluid (SBF) was used as the release medium. The pH was 7.4 and the temperature was 37°C.

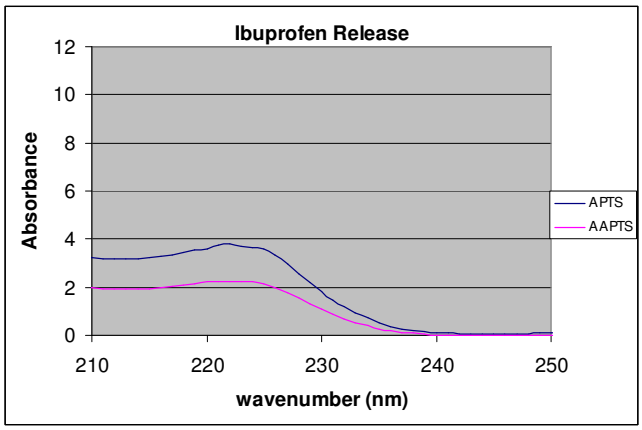

Figure 8. APTS and AAPTS release of ibuprofen

In the figure above APTS has a higher absorbance than AAPTS. This was expected

because APTS adsorbed more ibuprofen than AAPTS and, therefore, was expected to release more ibuprofen in the solution. The higher the absorbance the more ibuprofen is in the solution. This means that there was less ibuprofen in the functionalized material. The graphs in Figure 8 show the absorbance of ibuprofen from the analyzed supernatant. From the graphs, the concentration of ibuprofen in APTS and AAPTS was calculated. These studies assured that APTS and AAPTS did in fact adsorb and release ibuprofen. From these studies it is clear that modification of the surface of the mesoporous material MCM-41 affects the adsorption and release of ibuprofen.

CONCLUSION

The effect of functional groups on mesoporous materials on the adsorption rhodamine 6G and ibuprofen molecules was investigated. It was demonstrated that the mesoporous silica samples that were grafted with APTS adsorbed

ibuprofen more than AAPTS and the samples functionalized with MPTS and VTS did not adsorb any ibuprofen. There were stronger interactions between ibuprofen and the amine groups that resulted in the adsorption of ibuprofen by these groups. MPTS and VTS functionalized samples had a stronger interaction with the R6G molecules which resulted in a greater adsorption than the amine groups. Functionalization of MCM-41 played a major role in the adsorption and release of rhodamine 6G and ibuprofen.

FURTHER STUDIES

Further studies can be performed on these materials, such . Ttime release studies, may be performed on these samplesin order to to determine which grafted sample adsorbs and releases ibuprofen and R6G the most. Other functional groups may also be grafted to the walls of the mesoporous silica and different drugs may be tested in the adsorption and release studies. Grafting with more than one organosilane can be performed in

order to further control the adsorption and release of drugs and potentially create a gate in the mesoporous material that will open under certain conditions to adsorb or release drug molecules. ~~This can lead to the attachment of a gate to the mesoporous material.~~

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CHAPTER 2

Core-Shell Nanospheres with Multi-Shell Structures: Silica Cores Coated with Gold Nanoparticles and Silica Shells

Abstract

Nanoporous silica spheres were synthesized with procedures that included the addition of gold nanoparticles to the spheres followed by a silica coating, twice. This type of silica sphere has potential application in chemical adsorption and biosensing. The properties of these spheres can also be altered to be useful in applications involving infra-red radiation. This experiment demonstrated that multiple layer of gold nanoparticles and silica shells can be added to silica spheres which results in alterations of the properties of these spheres.

Introduction

Synthesis of inorganic nanomaterials with controllable structure, size and shape has become an important process in inorganic materials chemistry. Silver and gold nanoparticles with silica shell have drawn attention due to the possible uses in catalysis, surface enhanced Raman spectroscopy, biological diagnostic application, chromatography and optical devises.[1, 2] Recently the synthesis and use of multilayered nanostructures with multiple shells have become of great interest. An advantage of such silica core shells are that they can be used for optical applications due to its optical transparency.

Previous studies showed that the synthesis of gold nanoparticle silica shells can be potentially used for the encapsulation of drugs and for electrochemical applications. Van Blaaderen et. al. reported the coating of silica spheres with APTS in order to disperse coupling agents through the particle interior.[3] Others have used a metal centers coated with a silica shell due to the strong

absorption and optical properties of these materials.[4]

Silica spheres are also of increasing interest due to their potential applications such as in optical devices. Monodispersed spherical particles can be synthesized by self assembly. Additionally, silica nanoparticles are biocompatible and their surface ligands are easy to control.[5,6] The incorporation of nanoporous shells in the structures also provides a suitable materials for the encapsulation of drugs.[2] Nanoscale metal particles are widely used in various studies such as surface enhanced ~~spectrosopies~~spectroscopy, optoelectronics and optical stability. More specifically gold nanoparticles not only display good electronic and optical properties but are biocompatible and bioconjugation. This also allows extensive use in biological applications. In this study, amino organosilane groups were used to attach multiple layers of gold nanoparticles to silica core shell particles which were then surrounded by a layer of silica shell.

Experimental Methods

Materials

Tetraethoxysilane (TEOS), ammonium hydroxide, 3-aminopropyltrimethoxysilane (APTS), tetrahydrofuran (THF), isopropanol, hydrogen tetrachloroaurate ($HAuCl_4$), sodium borohydride and sodium citrate were all purchased from Sigma-Aldrich and used without further purification.

Synthesis of silica spheres

10 mL of ammonia solution was mixed with 100 mL ethanol and 3.6 g of water. The solution was stirred vigorously for 2 min. Then 2.80 g of

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tetraethoxysilane (TEOS) was added into the solution under moderate to strong stirring to hydrolyze TEOS for 3 hours. The solution turned white and milky. After 3hr the solution was centrifuged and the supernatant was carefully decanted. The precipitate was washed with a solution of 20 mL H_2O and 20 mL ethanol. The sides of the tube were scraped with a spatula before the solution was placed in a sonicator and washed because the paste stuck to the walls of the tube. This procedure was repeated. The precipitate was then sonicated and dispersed in a solution of 20 mL H_2O and 20 mL ethanol.

Functionalization of Silica Spheres

Half of the solution containing the synthesized silica spheres was then placed in a centrifuge and the supernatant (water/ethanol mixture) was decanted. Then 20 mL of toluene was added and the precipitate was dispersed in the solution. 3 mL of 3-aminopropyltrimethoxysilane (APTS) was then placed in the flask and the solution was stirred for 24 h at room temperature.

The precipitate was then washed with about 20 mL ethanol three times before it was dispersed in 20 mL tetrahydrofuran (THF). 0.01 M of 30 mL HCl was then added into the solution until complete precipitation of the colloidal nanoparticles occurred. The supernatant was decanted and the precipitate was then washed twice with ethanol. The functionalized spheres were then dispersed in 20 mL of water with a pH of 5.00.

Anchoring gold nanoparticles to the silica spheres

12 mL of the functionalized silica spheres were mixed with 20 mL of 5 mM $HAuCl_4$ and 0.2 ml of 0.025M sodium citrate solution. Then 2.4 mL of 10 mM sodium borohydride in 0.025M sodium citrate was added to the solution under stirring. After 30 seconds, stirring was stopped and the mixture was kept under static conditions for 2hr. The solution was then centrifuged. The supernatant was decanted and washed 4 times with 20 mL water. The particles were dispersed in 10 mL distilled water.

Formation of silica shell on silica spheres anchored with gold particles

TEOS was added to the gold particle silica spheres to create a thin silica shell coating. First 1.5 mL of silica spheres with gold nanoparticles was mixed with 5 mL isopropanol (2-propanol). 0.125 mL of ammonium hydroxide (30 wt%) was added to the solution and stirred for 20 minutes. Then over the course of 48 hrs 0.6ml of 20 mM tetraethylorthosilicate (TEOS) was added to the solution. 0.075 mL of TEOS in isopropanol was added every two hours for 8 hours. The solution was let to stir for 20 h then 0.075 mL of TEOS was again added over the course of 8 hrs. After ~ 12 h the solution was placed in a centrifuge and the supernatant was decanted and the spheres were washed with 15 mL of isopropanol (3 times) before they were dispersed in water.

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2nd layer of gold nanoparticles and silica shell

The procedures listed above were repeated. The silica spheres with silica shells were functionalized, then gold nanopaticles were anchored onto the surface of the shells, and another layer of the silica shell was then placed on top of the nanoparticles.

Results and Discussion

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) was used to analyze the spheres at various stages. The scanning scope used was a JEOL 5800LV and the transmission scope was a JEOL 2000EX.

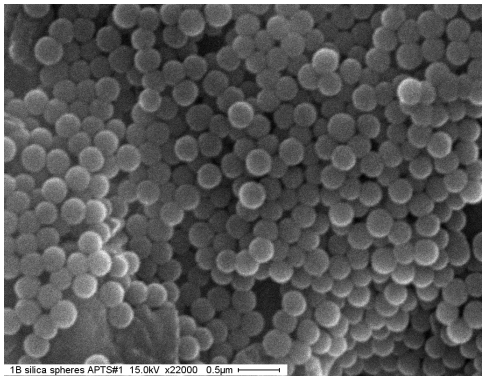
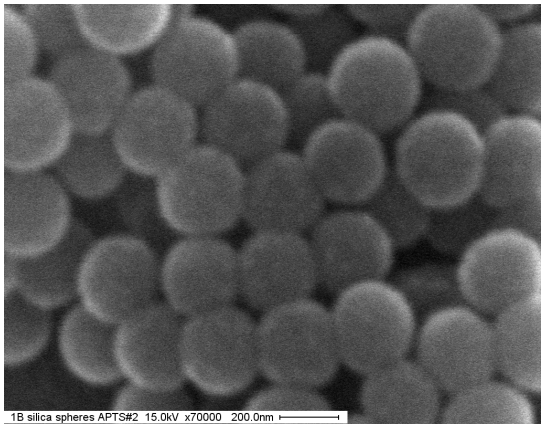


Figure 1. Scanning electron micrograph (SEM) displaying silica spheres after synthesis

A scanning electron microscopy (SEM) was used to analyze these samples. From this experiment the approximate size of the silica spheres was determined to be 250 nm. The spheres were ordered and spherical in shape.



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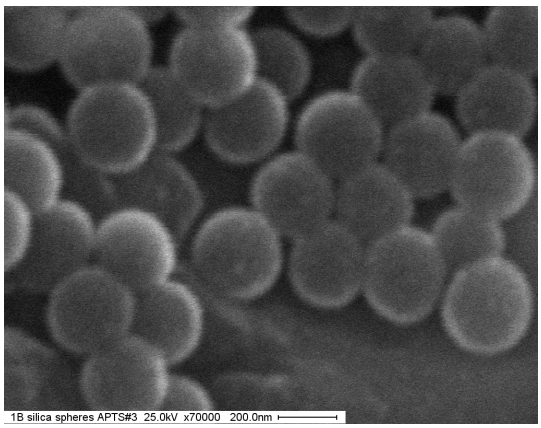

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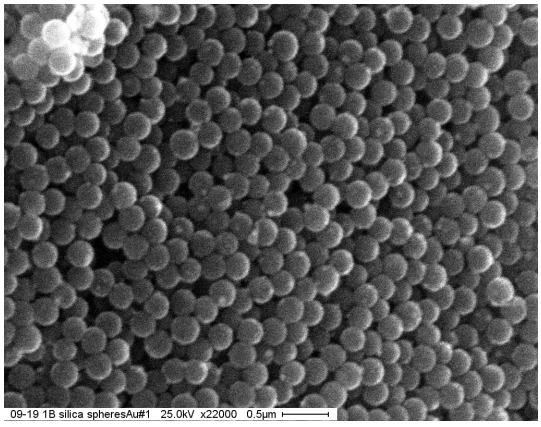
Figure 2. SEM images showing silica spheres functionalized with APTS

Figure 2a and 2b show the SEM images of spheres at 15.0 kV and 25.0 kV, respectively. The addition of functional groups is critical to the adhesion of the gold nanoparticles onto the silica surface.



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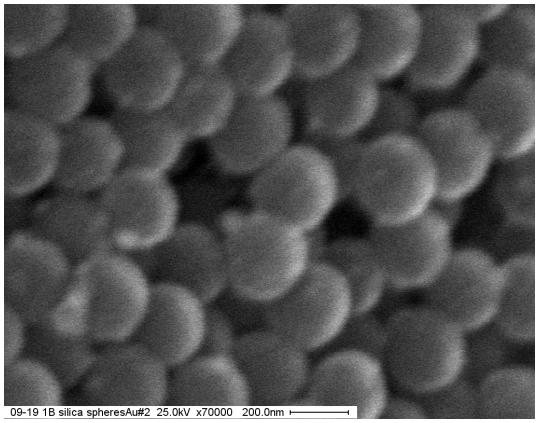

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3b.

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Figure 3. The above figures displays silica spheres with gold nanoparticles

The SEM images show that gold nanoparticles were successfully anchored onto the spheres (although the images do not appear to have good resolution). APTS was used to attach gold nanoparticles to the spheres. Figure 1 and Figure 2 display spheres with smooth surfaces, although Figure 2 shows functionalized spheres. Figure 3 displays apparent bumps on the spheres. The silica spheres are the darker images and the gold particles are the lighter and smaller substances that are attached to the silica spheres. Figure 3b shows a closer view of the spheres at 200 nm. The

difference between the silica and the gold is more apparent in this figure. After the first layer of gold was successfully attached to the spheres the gold nanaoparticles were encased in a silica shell. Some of the samples were also analyzed using transmission electron microscopy (TEM) (Figure 4).

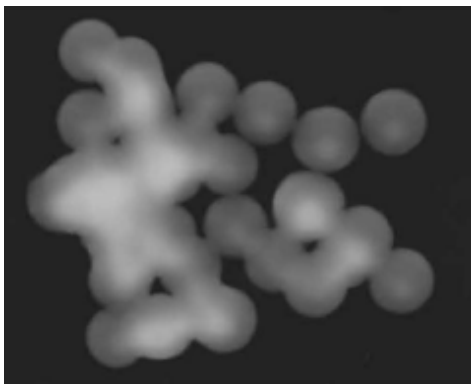
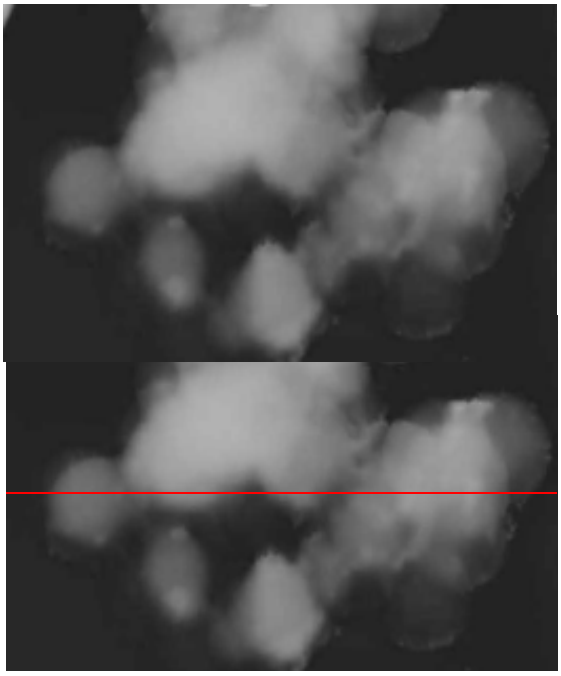


Figure 4. TEM image of silica spheres with the 1st layer of silica shell coating.

Compared to Figure 3, the spheres in Figure 4 have smooth surfaces. An interesting feature of these particular spheres is that there are some light spots inside the spheres. In Figure 3 the light spots were determined to be gold nanoparticles that were attached to the spheres. Since the difference between the spheres in Figure 3 and Figure 4 is the

silica shell, the light colored spots appear to be the gold nanoparticles. The spheres in Figure 4 were then functionalized (not shown) and a second layer of gold nanoparticles was then attached to the spheres.



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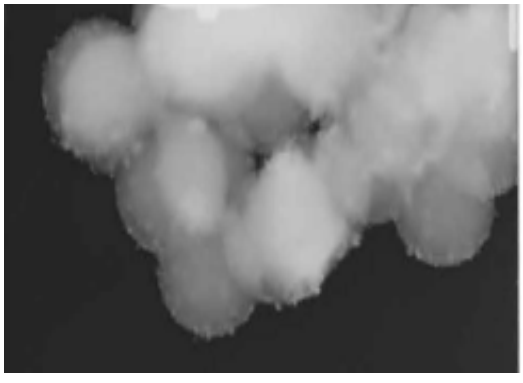

5b.

Figure 5. TEM images of silica spheres with 2nd layer of gold nanoparticles

Figure 5 clearly show the gold nanoparticles were anchored to the silica shell. The gold nanoparticles are light in color and create a rough surface on the spheres. Although it have been previously reported that gold nanoparticles can be anchored to silica spheres, this figure proves that the gold nanoparticles can be successively anchored to the silica spheres through the addition of silica shells.[1,2] This can also alter the properties of the silica spheres.

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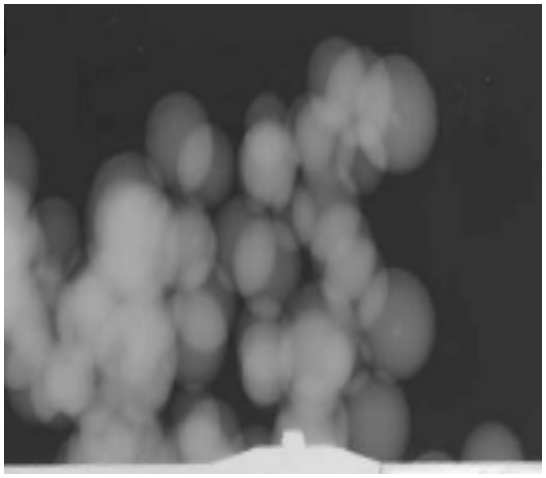

Figure 6. TEM image of silica sphere with 2nd coat of silica shell

The smooth surface of the spheres in Figure 6 show the addition of a second layer of silica shell. As in Figure 4, there are light spots that project from under the shells. This may indicate the presence of gold nanoparticles of the second layer, showing that they were encased in the silica spheres.

Conclusion

Successive addition of gold nanoparticles and silica shells was accomplished. APTS was an

adequate functional group to use to anchor the spheres onto the surface of the spheres. SEM and TEM images were sufficient instruments to show that alteration of the surfaces of the spheres from rough to smooth due to the addition of gold nanoparticles and silica shells, respectively. These spheres can be further tested to view its optical properties and have potential for bioimaging applications.

References

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